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RSCPublishing

ARTICLE

# One-pot catalytic asymmetric borylation of unsaturated aldehyde-derived imines; functionalisation to homoallylic boronate carboxylate ester derivatives

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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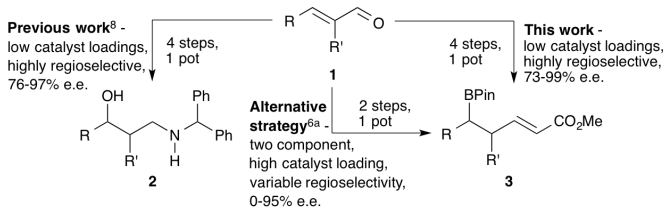
The β-borylation reaction of α,β-unsaturated aldehyde-derived imines, formed *in situ*, has been studied using a one-pot methodology, as a route to β-boryl aldehydes. The instability of the β-boryl aldehydes meant that derivatisation was required and routes to both acetal derivatives and homoallyicl boronates were examined. β-Boryl acetals were also found to be unstable, however, the formation of homoallylic boronate derivatives using an *in situ* imine hydrolysis-Wittig olefination protocol was found to be suitable, resulting in an efficient synthesis with high enantiomeric excesses.

## Introduction

Organoboron compounds have achieved many applications in several areas of organic chemistry, specifically as intermediates in asymmetric synthesis.[1] Consequently, much research has focused on the preparation of key chiral compounds, through the addition of boryl units to C=C bonds; *i.e.* borylation strategies. Within the scope of the various borylation strategies, a novel approach consisting of a conjugate addition of a boryl unit, from a diboron reagent, into an α,β-unsaturated system has been developed, *i.e.* the β-borylation reaction.[2] The diborylation (1,4-) of enones was first reported in the late 1990s by Marder *et al*.,[3] and subsequent hydrolysis led to β-boryl ketones. Since then, many organometallic and organocatalytic systems have been developed to prepare β-functionalised compounds[4] and the reaction has been developed into an enantioselective protocol through the use of chiral phosphines and *N*-heterocyclic carbenes, for example.[4c-d] Despite the major successes in this area, introduction of boryl moiety into α,β-unsaturated aldehydes still represents a substantial challenge because the desired 1,4-boryl addition can be competitive with 1,2-addition[5] and even under two component or organocatalytic conditions, regiocontrol is variable (*i.e.* see Alternative strategy, Scheme 1).[6] Also, β-boryl aldehydes are known to be unstable[6] making them problematic for further synthetic applications. In addition, current procedures for the catalytic asymmetric synthesis of β-boryl aldehydes suffer from a number of further problems, including variable enantiomeric excesses (generally low to moderate), and reactions require high catalyst and base loadings to produce even moderate yields.

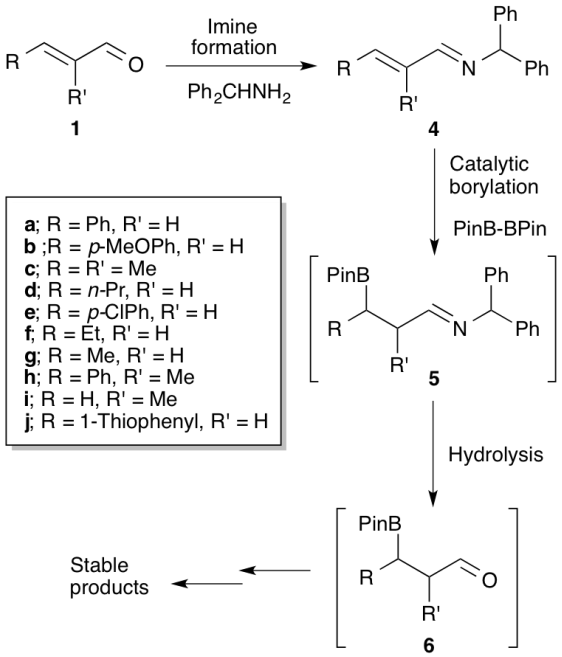
Over the last five years, we have been developing β-borylation methodologies which have been applied to the β-borylation of α,β-unsaturated imines.[7] We envisaged that one major advantage of this methodology should be that one could potentially overcome the major issue of regiocontrol in the borylation reaction α,β-unsaturated aldehydes **1** through the *in situ* formation of the corresponding α,β-unsaturated imine. Indeed, the formation of *N*-sterically hindered α,β-unsaturated aldimines can be used to promote a completely regioselective $C_\beta$-boryl-addition, resulting in the formation of β-boryl imines, which can be readily transformed into γ-amino alcohols **2** (*i.e.* see Previous work, Scheme 1)[8] and γ-diols.[9] However, it is also apparent that this effective methodology might be useful for solving the problems of regioselectivity of the borylation of α,β-unsaturated aldehydes compared with the alternative strategy[6] (Scheme 1) and the instability of the resulting β-boryl aldehydes. In addition, the development of a reliable, general, efficient, low catalyst loading [typically 3 mol% copper(I)-chiral bis-phosphine[8] compared with 20 mol% chiral secondary amine *and* 5 mol% copper(I) catalyst for the alternative strategy[6a]] and highly enantioselective synthesis of β-boryl aldehydes would make such species more amenable for use in synthesis. In this work, we report such a new process for the one-pot, *in situ* formation of β-boryl aldehydes, confirm their instability and hence, demonstrate their efficient synthesis by trapping through a Wittig reaction,[6] resulting in chiral homoallylic boronates **3** (see This work, Scheme 1).




**Scheme 1** Overall conversion of α,β-unsaturated aldehydes **1** to either chiral γ-amino alcohols **2** or homoallylic boronates **3**.

## Results and discussion

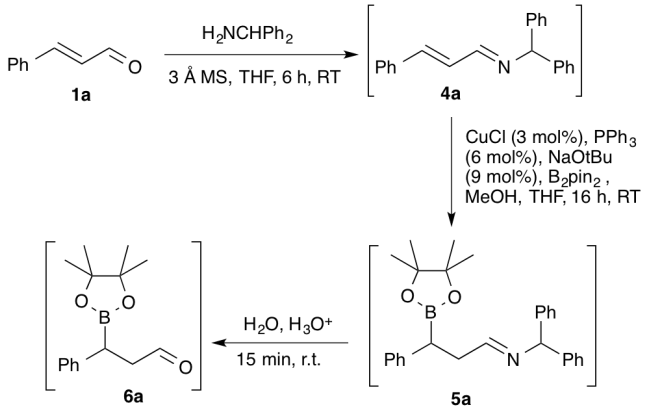
Homoallylic boronates **3** are attractive synthetic targets since there are a number of possibilities, such as the introduction of a second boryl unit, which can in turn be transformed into other functionalities leading to key building blocks for the synthesis of multifunctional, chiral compounds.[10] Hence, we initiated the development of a synthesis of such compounds through examining whether it was possible to convert α,β-unsaturated aldehydes **1** to the corresponding β-boryl aldehyde **6** *via* a one-pot, copper-catalysed, asymmetric 1,4-addition of $B_2pin_2$ to α,β-unsaturated aldehydes **1** *via* the corresponding imine **4** and β-boryl imine **5** (both formed *in situ*), followed by imine hydrolysis. The major question to be addressed was whether the β-boryl aldehyde **6** could be isolated and/or handled, and hence converted to subsequent derivatives, as outlined in Scheme 2.




**Scheme 2** Proposed synthetic pathway for the conversion of α,β-unsaturated aldehydes **1** to β-boryl aldehydes **6** *via* β-boryl imines **5**.

**Cu(I)-phosphine mediated β-borylation reaction of α,β-unsaturated aldehydes *via* β-boryl aldimines**

In order to explore the conjugate addition of $B_2pin_2$ to enals *via* the corresponding imine, cinnamaldehyde **1a** was chosen as the model substrate for developing optimal reaction conditions for the overall process outlined in Scheme 2, using the one-pot conditions outlined in Scheme 3.




**Scheme 3** Synthetic pathway for the Cu(I)-phosphine catalysed β-borylation reaction of cinnamaldehyde **1a** to derive the β-boryl aldehyde **6a**.

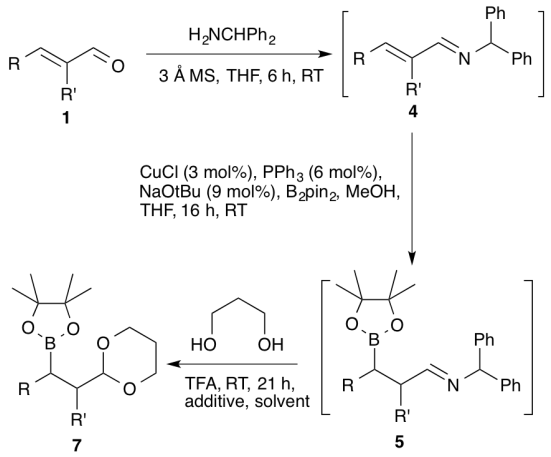
Hence, after imine formation (to give **4a**), catalytic borylation (*via* **5a**) and hydrolysis using aqueous HCl, compound **6a** was obtained in a crude form with high mass recovery and a notable absence of any starting aldehyde **1a**. However, after attempts to purify the crude product **6a**, a considerable amount of the starting aldehyde **1a** was obtained, graphically demonstrating the instability of β-boryl aldehydes of this type and their facile capability to re-eliminate the boryl unit, leading back to the starting unsaturated aldehyde **1a**. At present, the mechanism by which this de-borylation occurs is not clear; however, more importantly, this result highlighted that this approach was incapable of providing clean β-boryl aldehdye **6a** on which to perform further studies.

In order to examine possible means by which to avoid the instability problem associated with **6a** upon purification, the sequence shown in Scheme 3 was repeated with the *p*-methoxycinnamaldehyde-derived starting material **1b** to see if the electron donating group on the benzene might reduce the instability of the benzylic boryl product, *i.e.* **6b**. However, the β-boryl aldehyde **6b** was again isolated in high mass recovery in a crude form, yet during the purification process using flash chromatography on alumina or silica gel, only starting unsaturated aldehyde **1b** was obtained. Additionally, attempting to apply this methodology to a non-benzylic, and more substituted system such as tiglic aldehyde **1c**, surprisingly prevented the borylation reaction completely under the conditions outlined in Scheme 3. The use of a more reactive catalytic system (*i.e.* CuCl/P$^n$Bu$_3$ as described previously[4]) gave the target β-boryl aldehyde **6c** (starting from **1c**). However, it

was not possible to isolate the product in a pure form without decomposition back to the starting tiglic aldehyde **1c**. These results clearly corroborated literature reports that use of such β-boryl aldehydes are unstable relative to β-boryl ketones and esters.[3,11] However, in exceptional circumstances, β-boryl aldehydes containing highly hindered boronate esters can be isolated.[12]

In order to circumvent the instability of β-boryl aldehyde products **6**, the prolonged presence of the aldehyde functionality needed to be avoided. We therefore examined alternative solutions including deprotection of the β-boryl imine **5** followed by the formation of the corresponding acetal **7** directly in one-pot, as outlined in Scheme 4.




**Scheme 4** Synthetic pathway for the Cu(I)-phosphine catalysed β-borylation reaction of an unsaturated aldehydes **1** to derive the β-boryl acetals **7** (see Table 1).

Hence, unsaturated aldehydes **1b** and **d** were converted through to the corresponding β-boryl imines **5b** and **d** respectively, and then reacted with 1,3-propanodiol in the presence of an equivalent of TFA which efficiently gave the corresponding β-boryl acetals **7b** and **d** respectively (Table 1).

**Table 1** Reaction conditions screened for the synthesis of compounds **7**, as in Scheme 3[a]

| Entry | Solvent | Additive 3 Å MS | Conversion **7b**[b] (%) | Conversion **7d**[b] (%) |
|---|---|---|---|---|
| 1 | THF | Yes | 93 | 93 |
| 2 | THF | No | 68 | 96 |
| 3 | Toluene | Yes | 97 | 94 |
| 4 | Toluene | No | 87 | 96 |
| 5 | MTBE | Yes | 91 | 95 |
| 6 | MTBE | No | 81 | 97 |

[a]Reaction conditions: see Experimental. [b]Determined by $^1$H NMR on the crude reaction mixture.

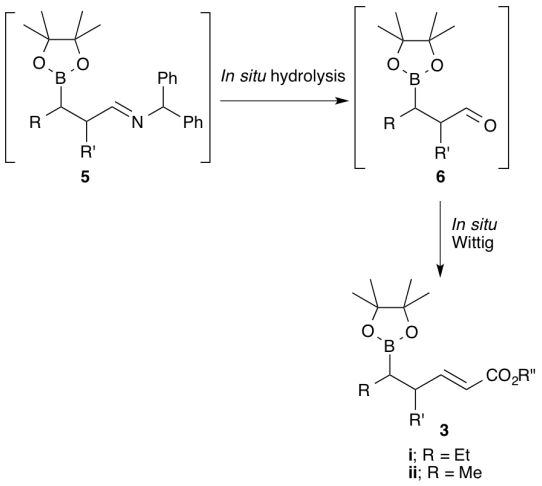
From the results presented in Table 1, it was concluded that the presence of 3 Å molecular sieves was necessary for the effective conversion, in one-pot, of the protonated imine directly to the corresponding acetals **7**, whereas the solvent polarity had little influence.

The conditions reported in Entry 3 (Table 1) for the synthesis of acetal **7b** could be reproduced on a larger scale; however, it was not possible to purify the product, as with the the β-boryl aldehydes **6**. All chromatographic purification attempts caused decomposition (presumably *via* facile acetal deprotection) resulting in sole re-isolation of the starting material **1b**.

The challenge of isolating either β-boryl aldehydes **6** or acetal derivatives **7** meant that alternative methods for direct derivatisation of the β-boryl imines **5** (*e.g. via in situ* generation of the corresponding β-boryl aldehydes **6**) was still required.

**Synthesis of chiral homoallylboronates *via* β-boryl aldimines**

A potential solution to the problematic isolation of β-boryl aldehydes **6** could entail direct Wittig olefination to the corresponding and synthetically versatile homoallylic boronates **3**, *i.e.* as outlined in Scheme 5.

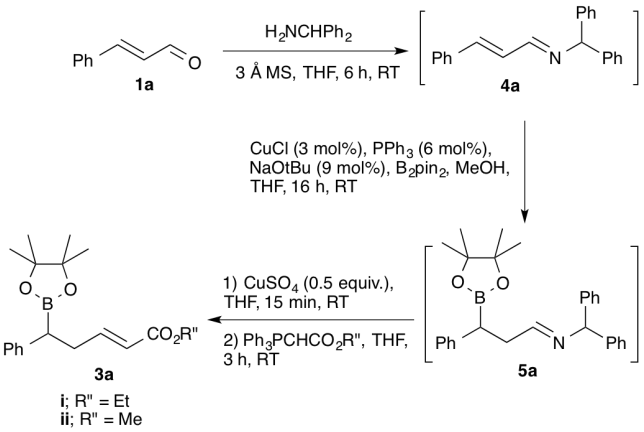



**Scheme 5** Proposed conversion of β-boryl imines **5** to the corresponding homoallylic boronates **3**.

Initially, Wittig reactions were attempted using β-boryl aldehydes **4a**, **4b** and **4d** (all formed *via* the acid hydrolysis conditions shown in Scheme 4), starting with the corresponding substrates unsaturated aldehydes **1a**, **1b** and **1d**. However, the subsequent Wittig did not cleanly convert the crude β-boryl aldehydes **6** to the corresponding homoallylic boronates **3** and only complex mixtures of products resulted. Seemingly, the instability of the β-boryl aldehydes **6** precludes the direct derivatisation of these systems under the Wittig reaction conditions. Hence, an alternative *in situ*, one-pot methodology was examined to see if it was possible to generate the β-boryl aldehyde and immediately trap through the Wittig reaction, which requires the use of a stabilised phosphorane to withstand the conditions required to hydrolyse the imine function of systems **5**. To that end and to test if that was feasible, unsaturated aldehyde **1a** was initially chosen, as outlined in Scheme 6, for examination of the *in situ* imine hydrolysis-

olefination reaction without isolation of the β-boryl aldehyde **6** intermediate.

**Scheme 6** One-pot, four-step methodology proposed for the synthesis of homoallylic boronate **3a** from cinnamaldehyde **1a**.




The overall conversion for the sequence shown in Scheme 5 was high, however, conditions needed to be optimised for chromatographic purification of the homoallylic boronate **3a** in order to provide matching isolated yields, as outlined in Table 2.

**Table 2** Optimisation of the conditions for the flash-column chromatography for the isolation of homoallylic boronate **3ai**

| Entry | Column support | Ratio, petroleum ether:EtOAc | Yield (%) |
|---|---|---|---|
| 1 | Silica gel | 20:1 | 35 |
| 2 | Silica gel | 2:1 (cold) | 60 |
| 3 | Silica gel | 3:2 (cold) | 64 |
| 4 | Silica gel | 13:1 (cold) | 55 |
| 5 | Alumina | 1:1 (cold) | 77 |
| 6 | Alumina | 2:1 (cold) | 36 |
| 7 | Florisil | 2:1 (cold) | 88 |
| 8 | Florisil | Gradient (cold) | 71 |

As shown in Table 2, the first attempts to purify compound **3a** (obtained in over 95% conversion in all cases) provided only a low yield (35%) using silica gel under standard room temperature conditions, along with a considerable proportion of starting unsaturated aldehyde **1a** (Entry 1, Table 2). Cooling the solvent and changing its polarity gave increased isolated yields (Entries 2-4, Table 2), again using silica gel, however, the highest yield was still only 64%. It was noted though that using either alumina or Florisil (entries 5-8, Table 2) gave no decomposition of the homoallylic boronate **3a**, and high yields could be obtained, *i.e.* up to 88%. Based on these results, it was clear that purification of the homoallylic boronates **3** was possible, however, it was felt that the yields obtained needed to be optimised further to reduce the presence of starting unsaturated aldehyde **1a**, *i.e.* by ensuring the complete hydrolysis of the intermediate imine **4** and a fast, efficient Wittig reaction to trap the intermediate β-boryl aldehyde **6**. Each of these steps was further screened for different conditions, as reported in Table 3.

**Table 3** Reaction conditions screened for the hydrolysis of imine **5a** and Wittig reaction to give **3a**[a]

| Entry | $CuSO_4$ equiv. | Ylide (equiv.) | Time (h) | Temp. (°C) | **1a**[a] |
|---|---|---|---|---|---|
| 1 | 0.5 | $Ph_3PCHCO_2Et$ (1.3) | 3 | RT | Yes |
| 2 | 1.0 | $Ph_3PCHCO_2Et$ (1.3) | 4 | 40 | Yes |
| 3 | 1.0 | $Ph_3PCHCO_2Et$ (1.5) | 8 | RT | Yes |
| 4 | excess (sat.) | $Ph_3PCHCO_2Me$ (1.1) | 4 | RT | Yes |
| 5 | 2.0 | $Ph_3PCHCO_2Me$ (1.5) | 5 | RT | No |
| 6 | 2.0 | $Ph_3PCHCO_2Me$ (1.5) | 5 | 40 | Yes |

[a] Residual **1a** was observed by $^1H$ NMR on the reaction crude mixture.

Table 3, Entry 5 shows that using 2 equivalents of copper(II) sulfate gave complete β-boryl imine **5a** hydrolysis and efficient Wittig trapping occurred with 1.5 equivalents of ylide, and hence transformation into **3a**. In this case, there was no starting unsaturated aldehyde **1a** remaining in the crude reaction mixture. Hence, with these reaction conditions defined, the next targets were to apply these reaction sequences for the asymmetric borylation reaction[7,8] using (*R*)-DM-BINAP **L1** for the conversion of unsaturated imines **4** to the corresponding β-boryl imines **5** to give the absolute stereochemistry shown in Scheme 6.[8] This would then be followed by the *in situ* hydrolysis, Wittig trapping process on a range of different unsaturated aldehydes. Scheme 7 shows the general pathway employed for transformation of the unsaturated aldehydes **1**, with the respective yields and e.e.s summarized in Table 4.

Table 4, Entry 1 exemplifies the successful synthesis of compound **3aii** from cinnamaldehyde **1a** using the sequence outlined in Scheme 7. Hence, homoallylic boronate **3aii** was obtained in a 54% isolated yield over the four-step sequence, with an e.e. of 98% when using (*R*)-DM-BINAP **L1** in place of triphenylphosphine in the copper(I)-mediated borylation step. This methodology also worked well on a wider range of α,β-unsaturated aldehydes **1** to derive for the corresponding homoallylic boronates **3** with e.e.s varying from 73 to >98%. The isolated yields, considering the number of steps in this one-pot protocol, were moderate to good.

**Scheme 7** Enantioselective synthetic pathway proposed for the synthesis of homoallylic boronates **3** from the corresponding unsaturated aldehydes **1**

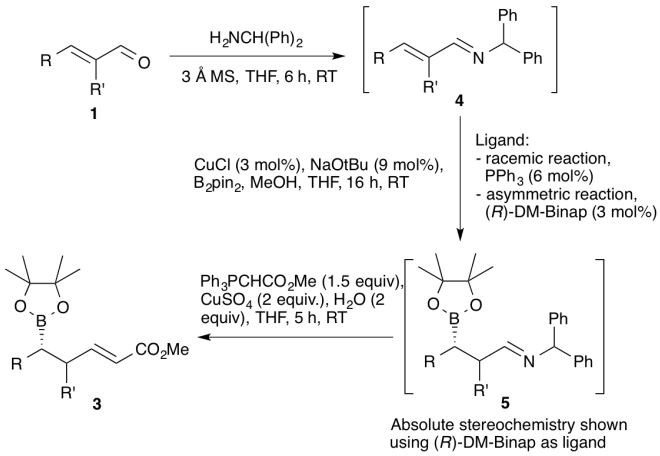
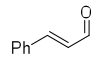
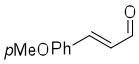
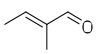
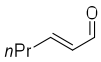
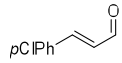
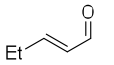
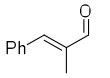
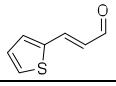



**Table 4** Overall isolated yields and e.e.s for the conversion of unsaturated aldehydes **1** to homoallylic boronates **3**

| Entry | Unsaturated aldehyde **1** | Ligand | Yield **3** (%) | e.e. **3** (%)[f] |
|---|---|---|---|---|
| 1 |  **1a** | **L1** | 46 | 98 |
| 2 | | $PPh_3$ | 54 | |
| 3 |  **1b** | **L1** | 40 | 87 |
| 4 | | $PPh_3$ | 27 | |
| 5 |  **1c** | **L1** | 20 | [-][c] |
| 6 | | $PPh_3$ | 60[b] | |
| 7 |  **1d** | **L1** | 45 | 91 |
| 8 | | $PPh_3$ | 74 | |
| 9 |  **1e** | **L1** | 38 | 98 |
| 10 | | $PPh_3$ | 54 | |
| 11 |  **1f** | **L1** | 70 | 73 |
| 12 | | $PPh_3$ | 54 | |
| 13 |  **1g** | **L1** | 65 | 80 |
| 14 | | $PPh_3$ | 34 | |
| 15 |  **1h** | **L1** | 19 | [-][c] |
| 16 | | $PPh_3$ | 29 | |
| 17 |  **1i** | $PPh_3$ | 36 | - |
| 18[e] |  **1j** | $PPh_3$ | - | - |

[a] Absolute stereochemistry as shown in Scheme 7 where relevant and on the basis of previous reports (see references 8). [b]Obtained as an 1:4 mixture of *syn*:*anti* diastereoisomers. [c]Not determined. [d]Conversion only and with a 50 °C reaction temperature. [e]β-Borylation proved efficient (measured by NMR), but subsequent transformation *via* Wittig chemistry failed to form the resulting compound **3j**. [f]Measured by chiral HPLC (see ESI).

Despite the successful application of this methodology to a range of substrates, as outlined in Tables 4, not all substrates were suitable for the borylation reaction, *i.e. p*-nitrocinnamaldehyde was found to be unsuitable for imine formation, resulting only in Michael addition products rather than imine formation. In addition, acrolein was also unsuitable, since attempts to use it as a starting material resulted only in polymerisation products. However, and perhaps surprisingly, methacrolein did undergo the imine formation to give **4i**, borylation to give **5i**, hydrolysis and Wittig trapping, as shown in Table 4, Entry 9, to give homoallyic boroate **3i**.

The impact of the different unsaturated aldehyde substituents on the overall process is interesting to note. Highest e.e.s are obtained with R = aryl functions, such as in Entries 1, 2 and 5 (Table 4). With alkyl substituents, there was evidence of steric effects operating, and hence, a R = propyl function (Entry 4, Table 1) gave higher e.e. than the corresponding ethyl or methyl groups (Entries 6 and 7, Table 4 respectively). The influence of a substituent R' in the starting unsaturated aldehyde **1** was also interesting and gave mixed results. Hence, tiglic aldehyde **1c** Table 4, Entry 3) and α-methyl-cinnamaldehyde **1h** (Table 4, Entry 8) provided the corresponding imines **4** smoothly. However, there was a significant effect of the R methyl groups in both cases, with the boryl conjugate addition step being slower, and especially when the chiral diphosphine ligand was used. This was reflected in slower reactions and low yields in both cases and in fact, for the α-methyl-cinnamaldehyde substrate **1h**, the β-borylation did not take place at room temperature and the reaction needed to be performed at 50 °C. Because of this, the efficiency of the asymmetric step was not determined, however, the diastereocontrol was the same for both the achiral and chiral phosphines, *i.e.* a 1:4 mixture of *syn*:*anti* diastereoisomers (Table 4, Entry 8). For the tiglic aldehyde **1c** (Table 4, Entry 3), homoallylic boronate **3c** was obtained in 20% isolated yield as a mixture of diastereoisomers which was not readily separable by chiral HPLC using several different columns (including OD, OJ-H, AS and AD and a range solvent elution systems). However, the relative stereochemistry from the racemic reaction ($PPh_3$ as ligand) was assigned, and was in agreement with previous reports, *i.e.* as a 1:4 mixture of *syn*:*anti* diastereoisomers.

This methodology represents an effective enantioselective protocol providing good to excellent *e.e.*s in the asymmetric variant. However, the lower enantiomeric excesses obtained from hexenal **1f** and pentenal **1g** (Entries 6 and 7, Table 4) prompted us to further examine possible methods of improving the asymmetric induction. Considering the key role of methanol as the protonating additive in the catalytic cycle corresponding of the β-borylation step as originally developed by Yun *et al.*,[13] we decided to examine the use of an alcohol as both the reaction medium and protonating agent, wondering if a more hindered alcohol might improve the enantioselectivity while maintaining a solvent polarity similar to THF for solubility purposes. Hence, isopropanol was employed in place of THF in Scheme 7, *i.e.* as sole solvent for the entire reaction sequence,

from imine formation to imine hydrolysis-Wittig trapping, with no methanol addition. The results are summarised in Table 5 and 5.

**Table 5** Enantioselective synthesis of homoallylic boronates **3** from unsaturated aldehydes **1** in $^{i}$PrOH.

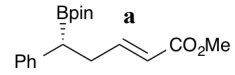
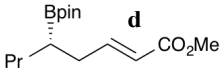
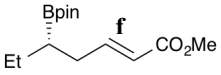
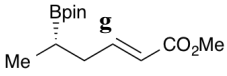
| Entry | Substrate **1** | Product **3** structure | Yield (%) | E.e. (%) |
|---|---|---|---|---|
| 1 | **a** |  | 66 | 99 |
| 2 | **d** |  | 50 | 96 |
| 3 | **f** |  | 65 | 83 |
| 4 | **g** |  | 37 | 82 |

**Table 6** Comparison of the imine formation reaction time between $^{i}$PrOH and THF/MeOH.

| Entry | Substrate **1** | Imine formation time (h) | |
|---|---|---|---|
| | | $^{i}$PrOH | THF |
| 1 | Cinnamaldehyde **1a** | 2.5 | 6 |
| 2 | 2-Hexenal **1d** | 1 | 8 |
| 3 | 2-Pentenal **1f** | 1 | 8 |
| 4 | Crotonaldehyde **1g** | 1 | 6 |

Reaction followed *in situ* by ReactIR (see ESI).

The result of this solvent change (Tables 5 and 6) was considerably beneficial in two aspects: 1) Improved asymmetric induction was observed when the homoallylic boronates **3** were isolated. In fact, both hexenal and pentenal-derived products **3d** and **3f** showed e.e.s of 96 and 83% respectively (Table 5). Indeed, even crotonaldehyde **1g** could be employed effectively in this asymmetric process to give the corresponding homoallylic boronate **3g** in 82% e.e.; 2) Monitoring the imine formation step (Scheme 7) by *in situ* IR spectroscopy (ReactIR)[7d] in IPA (Table 6) showed that it was considerably faster that using the standard THF-based system. It is noteworthy that not only were imine formations faster in IPA, and e.e.s higher, but in many cases, the imines crystallised and clean crystalline compounds suitable for X-ray analysis were obtained.

## Conclusions

In summary, an efficient one-pot methodology for the synthesis of chiral homoallylic boronates has been developed (e.e.s up to 99%). During this work, the significant challenge of working with α,β-unsaturated aldehydes were met in terms of controlling the competitive 1,2- *vs*. 1,4-addition. Additionally and more importantly, the even greater challenge of handling β-boryl aldehydes has been circumvented. In particular, it was confirmed that β-boryl aldehydes are indeed unstable and especially under chromatographic purification conditions, leading to de-borylation. The solution presented herein is a mild, efficient derivatisation process involving an *in situ* copper(II) sulfate-based imine hydrolysis followed by Wittig trapping of the resulting aldehyde. Additionally, the use of $^{i}$PrOH as a reaction medium for all steps in the one-pot sequence resulted in faster reactions and higher e.e.s when compared to previous attempts using THF.

The further exploitation of the chiral homoallylic boronates as platforms in synthetic chemistry is under examination and will be reported in due course.

## Experimental

**General experimental**

All the reactions reported herein were performed under air unless otherwise specified. The reagents were purchased directly from standard chemical suppliers and used as received from the supplier without further purification. All solvents were used as received from the supplier, except THF and MeOH which were stored over dehydrating reagents and were deoxygenated before use. Molecular sieves, 3 Å 1-2 mm beads, were supplied from Alfa Aesar, and stored at 220 ºC (>48 h).

Deuterated chloroform ($CDCl_3$) was used as solvent for routine NMR measurements. $^{1}$H NMR spectra were recorded on a Varian-Mercury 400 MHz spectrometer, operating at ambient probe temperature unless specified elsewhere. Coupling constants (*J*) are given in Hz, and the multiplicity of the NMR signals is described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). $^{13}$C NMR spectra were recorded on Varian Brüker Avance 400 MHz. $^{1}$H NMR and $^{13}$C NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane, references to the chemical shifts of residual solvent resonances. $^{11}$B NMR spectra were recorder on a Varian Brüker Avance 400 MHz operating at a frequency of 128 MHz and the chemical shifts are reported in ppm (δ) relative to $BF_3(CH_3)_2O$.

Mass spectra for liquid chromatography mass spectrometry (LCMS) were obtained using a Waters (UK) TQD mass spectrometer (low resolution ESI+, electrospray in positive ion mode, ES+) unless stated elsewhere. Accurate mass spectrometry was obtained on a Finnigan LTQ-FT.The purification of the reaction crudes was performed using flash column chromatography, which was carried out using different supports; Silica gel as supplied from Sigma-Aldrich (230-400 mesh, 40-63 μm, 60 Å); activated magnesium silicate Florisil® (100-200 mesh, 289 $m^2$/g) and monitored in both cases using TLC analysis using POLYGRAM® SIL G/UV254 (40 x 80 mm) TLC plates; and activated neutral aluminium oxide Alumina and monitored using TLC-PET foils of aluminium oxide with fluorescent indicator 254 nm (40 x 80 mm). In all cases the TLC plates were visualised under a UV lamp

operating at short (254 nm) and long (365 nm) wavelength ranges. Visualisation was aided by dipping plates into an alkaline potassium permanganate solution.

For the imine formation studies reactions were monitored by in situ IR spectroscopy experiments (ReactIR), the instrument which these experiments were carried out with is a ReactIR 4000 equiped with MCT detector; ConcIRT window = 1900-900 $cm^{-1}$. Advance setting: Laser WN = 7901-415 $cm^{-1}$; Apodization = Happ General. Probe: Prob A DiComp (Diamond) connected *via* K6 Conduit (16 mm prob); Sampling 4000-6500 at 8 $cm^{-1}$ resolution; Scan option: auto select, gain 2X.

**Copper(I)-phosphine mediated β-borylation reaction of α,β-unsaturated aldehydes**

General procedure for the synthesis of β-boryl aldehydes **6a-c**

α,β-Unsaturated imine **4** was formed *in situ* from the reaction between enal (0.5 mmol) and amine (0.5 mmol) stirred in THF (2.0 mL) and oven-dried 3 Å MS (0.5 g) for 6 h. After 6 h, an aliquot of the solution containing the *in situ*-formed imine **2** (2.0 mL, 0.5 mmol) was transferred to a Schlenk-tube (under argon) containing CuCl (1.5 mg, 0.015 mmol, 3 mol%), $PPh_3$ (32.0 mg, 0.12 mmol, 6 mol%), NaO*t*Bu (4.3 mg, 0.045 mmol, 9 mol%) and $B_2pin_2$ (104.0 mg, 0.55 mmol, 1.1 equiv.). After 5 min, MeOH (50.0 μL, 1.25 mmol, 2.5 equiv.) was added to the solution and the reaction was stirred overnight. The solution containing the β-boryl mine **5** was transferred into a round bottom flask, then $H_2O$ (5.0 mL) were added into the solution. The reaction mixture was stirred during 1 h at room temperature. The resulting solution was partitioned with EtOAc (60.0 mL). The organic layer was washed with HCl 5% (3 x HCl) and with $H_2O$ (3 x $H_2O$) until the aqueous layer had a neutral pH. The organic phase was separated and dried over $MgSO_4$. After filtration the organic phase removed under reduced pressure to yield crude of the aldehyde 4a-c. Purification by silica gel chromatography using a gradient of solvent mixture of petroleum ether: EtOAc in the ratios 9:1, 7:3, 2:1, 1:1, 3:2, 2:3, 0:1.

**General procedure for the synthesis of β-boryl acetals** 7 **via β-boryl imines**

An aliquot containing the β-boryl aldimine **5** (2.0 mL, 0.5 mmol) was transferred into a test tube containing the solvent followed by the addition of 1,3-propanediol (36.0 μL, 0.5 mmol, 1 equiv.) and TFA (38.0 μL, 0.5 mmol, 1 equiv.). The reaction mixture was stirred during 24 h at RT.

**Synthesis of chiral homoallylboronates *via* β-boryl imines**

General procedure for the synthesis of homoallylic boronates **3** from the β-boryl aldehyde **6**. An aliquot containing the β-boryl aldehyde **6a** (0.94 g, 4 mmol) was transferred into a round bottom flask containing THF (40 mL) followed by the addition of (carbethoxymethylene)triphenylphosphorane (1.7 g, 1.3 equiv.). The reaction mixture was stirred for 3 h at room temperature. The resulting solution was partitioned with EtOAc (60.0 mL) and brine (15.0 mL). The organic phase was separated and dried over $MgSO_4$. After filtration the organic phase removed under reduced pressure to yield crude of the homoallylboronate **3a**.

**General procedure for the one-pot, four-step enantioselective synthesis of homoallylic boronates** 3 **from α,β-unsaturated aldehydes** 1

Into a round bottom flask containing oven-dried 3 Å molecular sieves (5.0 g), were added solvent (20.0 mL), enal (5.0 mmol) and benzhydrylamine (1.0 equiv). The reaction mixture was stirred at room temperature leading to the imine-derived unsaturated imine **4**. To a Schlenk tube (under Ar) containing CuCl (12.0 mg, 0.15 mmol, 3 mol%), $PPh_3$ (63.0 mg, 0.3 mmol, 6 mol%) or DM-BINAP **L1** (88.0 mg, 0.15 mmol, 3 mol%), NaO*t*Bu (35.0 mg, 0.45 mmol, 9 mol%) and $B_2pin_2$ (1.02 g, 5 mmol, 1.0 equiv.), was added an aliquot of the solution containing unsaturated imine **4** (16.0 mL). Note that in the case of the use of THF as solvent after 5 minutes stirring the mixture, MeOH (2.5 equiv., 0.4 mL) was added. After 16 h, the resulting β-boryl imine **5a-h** was transferred into a round bottom flask then methyl(triphenylphosphoranylidene)acetate (1.5 equiv., 2.0 g) was added, after 5 minutes $CuSO_4$ (2.0 equiv., 1.3 g) was added along with $H_2O$ (10.0 equiv., 0.7 mL). The mixture was stirred for 5 h at room temperature. The resulting solution was partioned between EtOAc and brine. The aqueous layer was extracted further with EtOAc (3 x EtOAc). The organic phase was separated and washed with a $CuSO_4$ saturated solution (3 x $CuSO_4$), dried over $MgSO_4$. The crude reaction mixture was purified by a silica gel chromatography (hexane: methanol, 20:1 and 10:1 as eluent) which gave the pure homoallylic boronates **3**.

*Ethyl (E)-5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enoate* **3ai**

Compound **3ai** was obtained as a yellow oil (906 mg, 55%): IR (neat) $\nu_{max}$ 2978 (m), 1718 (m), 1653 (s), 1365 (m), 1326 (m), 1265 (m), 1167 (s), 1140 (m), 1030 (s), 966 (s), 849 (s), 696 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42-7.12 (m, 5H), 6.96 (dt, *J* 15.7, 6.9 Hz, 1H), 5.82 (dt, *J* 15.6, 1.4 Hz, 1H), 4.15 (q, *J* 7.1 Hz, 2H), 2.73 (m, 1H), 2.53 (m, 1H), 2.46 (m, 1H), 1.26 (t, *J* 7.1 Hz, 3H), 1.21 (s, 6H), 1.18 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 166.5 (*C*OOR), 148.3, 141.6 (*C*H=CH-COOR), 128.6, 128.3, 125.4, 121.9 (CH=*C*H-COOR), 83.6, 60.0 (O-$CH_2CH_3$), 35.1, 24.5 (*C*-CH=C), 21.4; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 32.7; LRMS (ESI+) m/z [M+H] 354.1 (100%), 332.1 (35%), 329.9 (23%), 317 (21%), 313.9 (8%); Chiral HPLC conditions OJ-H-CHIRALCEL column (250 x 4.60 mm) fitted with guard cartridge (50 x 4.6 mm), 25 ºC, 0.2 mL/min, 210 nm, hexane: $^i$PrOH (99:1), $t_R$ *(S)* = 35.6 min, $t_R$ *(R)* = 39.7 min. All spectroscopic and analytical data were identical to those reported in the literature.[6]

*Methyl (E)-5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-enoate* **3aii**

Compound **3aii** was obtained as a yellow oil (680 mg, 54%) with a $R_f$ = 0.25: IR (neat) $\nu_{max}$ 2980 (m), 1720 (l), 1656 (m),

1438 (m), 1370 (l), 1328 (l), 1270 (l), 1194 (m), 1140 (l), 1032 (s), 966 (m), 848 (l), 752 (l), 700 (l); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.14 (m, 5H), 7.02 – 6.94 (m, 1H), 5.86 – 5.82 (d, *J* 16 Hz, 1H), 3.71 (s, 3H), 2.82 – 2.72 (m, 1H), 2.62 – 2.54 (m, 1H), 2.51 – 2.47 (m, 1H), 1.23 (s, 6H), 1.20 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.0 (*C*OOR), 148.2, 141.7 (*C*H=CH-COOR), 128.8, 128.3, 125.7, 121.8 (CH=*C*H-COOR), 83.6, 51.7, 35, 24.9 (*C*-CH=C); $^{11}$B NMR (128 MHz, $CDCl_3$) δ 32.7; LRMS (ESI +) m/z [M+H] 318.3 (100%), 317.7 (21%), 317.8 (33%); HRMS (ESI+) m/z calculated $C_{18}H_{26}BO_4$ [M+H] 316.1960, found 316.1953; Chiral HPLC conditions OJ-H-CHIRALCEL column (250 x 4.60 mm) fitted with guard cartridge (50 x 4.6 mm), 25 ºC, 0.2 mL/min, 210 nm, hexane: $^i$PrOH (99:1), $t_R$ = 41.9 min *(S),* $t_R$ = 45.8 min *(R)*. All spectroscopic and analytical data were identical to those reported in the literature.[2]

*Methyl (E)-5-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enoate* **3bii**

Compound **3bii** was obtained as a yellow oil (367 mg, 53%): IR (neat) $\nu_{max}$ 2984 (m), 2886 (s), 1722 (l), 1658 (m), 1650 (m), 1630 (s), 1510 (l), 1442 (m), 1368 (m), 1328 (m), 1248 (l), 1180 (m), 1140 (l), 1124 (s), 1042 (m), 1016 (s), 970 (m), 852 (m), 850 (m), 760 (m), 744 (m), 710 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.18 – 6.89 (m, 4H), 6.85 – 6.81 (dt, *J* 8, 1H), 5.82 (d, *J* 15, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.69 (m, 1H), 2.54 (m, 1H), 2.43 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 167.0 (*C*OOR), 157.6, 148.9 (*C*H=CH-COOR), 133.5, 129.1, 121.4 (CH=*C*H-COOR), 113.9, 83.5, 55.1, 51.3, 35.3, 24.6, 24.5; $^{11}$B (128 MHz, $CDCl_3$) δ 32.6; LRMS (ESI +) m/z [M+H] 368.9 (100%), 364.0 (37%), 347.1 (35.5%), 363.5 (12%); HRMS (ESI+) m/z calculated $C_{19}H_{27}BO_5$ [M+H] 346.2066 found 346.2066; Chiral HPLC conditions OJ-H-CHIRALCEL column (250 x 4.60 mm) fitted with guard cartridge (50 x 4.6 mm), 25 ºC, 0.8 mL/min, 210 nm, hexane: $^i$PrOH (97:3), $t_R$ = 12.6 min *(R),* $t_R$ = 14.7 min *(S)*.

Methyl (*E*)-4-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-2-enoate **3cii**

Compound **3cii** was obtained as a yellow oil (161 mg, 60%): IR (neat) $\nu_{max}$ 2986 (m), 2904 (S), 2336 (l), 2370 (l), 1726 (l), 1704 (m), 1466 (m), 1464 (m), 1382 (l), 1380 (l), 1320 (l), 1308 (m), 1240 (m), 1144 (l), 1032 (m), 1030 (m), 954 (s), 848 (m), 750 (s), 704 (m), 670 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.83 (m, 1H), 5.80 (d, *J* 16, 1H), 3.74 (s, 3H), 1.58 (s, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.09 (dd, *J* 6.8, 2.6 Hz, 3H), 0.93 (d, *J* 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 167.2 (*C*OOR), 154.9 (*C*H=CH-COOR), 128.3, 127.2, 119.7 (CH=*C*H-COOR), 83.1, 51.2, 39.2, 24.8 (C-CH=C), 19.0, 13.6; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 33.8; LRMS (ESI +) m/z 269.2 (100%), 237.1 (95%), 291.2 (66%); [M+H] HRMS (ESI+) m/z calculated $C_{14}H_{25}BO_4$ [M+H] 268.1960 found 268.1982.

*Methyl (E)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-enoate* **3dii**

Compound **3dii** was obtained as a yellow oil (832 mg, 74%) with a $R_f$ = 0.33: IR (neat) $\nu_{max}$ 2934 (m), 1722 (l), 1656 (s), 1434 (s), 1386 (m), 1316 (l), 1262 (m), 1140 (l), 1046 (s), 982 (m), 860 (m), 752 (l), 696 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.03 - 6.95 (m, 1H), 5.86 – 5.82 (d, *J* 16Hz, 1H), 3.73 (s, 3H), 2.83 – 2.66 (m, 1H), 2.38 – 2.21 (m, 1H), 2.38 – 2.21 (m, 1H), 1.61 (s, 6H), 1.35 (s, 6H), 0.92 – 0.89 (t, *J* 7.2, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.1 (*C*OOR), 149.8, 121.2 (CH=*C*H-COOR), 83.2, 51.3, 33.7, 33.0, 24.8 (*C*-CH=C), 22.0, 14.30; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 33.9; LRMS (ESI +) m/z [M+H] 283.2 (100%), 282.1 (12%), 284.5 (10%); HRMS (ESI+) m/z calculated $C_{15}H_{28}BO_4$ [M+H] 282.2117, found 282.2130; Chiral HPLC conditions OD-CHIRALCEL column (250 x 4.60 mm) fitted with guard cartridge (50 x 4.6 mm), 25 ºC, 0.7 mL/min, 210 nm, hexane: $^i$PrOH (99.5:0.5),,$t_R$ = 8.7 min *(S),* $t_R$ = 11.1 min *(R)*.

*Methyl (E)-5-(4-chlorophenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enoate* **3eii**

Compound **3eii** was obtained as a yellow oil (377 mg, 54%): IR (neat) $\nu_{max}$ 2982 (m), 2970 (s), 1722 (l), 1658 (m), 1492 (l), 1438 (m), 1372 (m), 1332 (m), 1274 (m), 1202 (m), 1200 (m), 1142 (l), 1092 (m), 1012 (m), 970 (m), 844 (m), 842 (m), 796 (s), 702 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.11 (m, 4H), 7.03 – 6.89 (m, 1H), 5.84 – 5.79 (dt, *J* 16, 1H), 3.71 (s, 3H), 2.79 – 2.68 (m, 1H), 2.59 – 2.49 (m, 1H), 2.48 – 2.44 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.8, 148.1, 147.7, 140.1, 131.1, 129.5, 128.4, 127.5, 121.7, 83.7, 51.1, 34.8, 33.6, 33.3, 30.2, 24.5; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 32.7; LRMS (ESI +) m/z [M+H] 373.5 (100%), 351.1 (91%), 372.6 (80%), 375.1 (75%); HRMS (ESI+) m/z calculated $C_{18}H_{25}BO_4Cl$ [M] 350.1571 found 350.1573; Chiral HPLC conditions OD-CHIRALCEL column (250 x 4.60 mm) fitted with guard cartridge (50 x 4.6 mm), 25 ºC, 0.8 mL/min, 210 nm, hexane: $^i$PrOH (99:1), $t_R$ = 10.7 min *(S),* $t_R$ = 13.0 min *(R)*.

*(E)-Methyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate* **3fii**

Compound **3fii** was obtained as a yellow oil (746 mg, 70%) with a $R_f$ = 0.1: IR (neat) $\nu_{max}$ 2980 (l), 2982 (l), 2914 (m), 1726 (l), 1656 (m), 1440 (m), 1388 (l), 1322 (l), 1266 (l), 1200 (s), 1138 (l), 1048 (s), 974 (m), 846 (m), 760 (m), 744 (s); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.91 (dt, *J* 15.6, 7.2 Hz, 1H), 5.84 – 5.88 (dt, *J* 15.6, 1.5 Hz, 1H), 3.70 (s, 3H), 2.36 – 2.18 (m, 2H), 1.50 – 1.36 (m, 2H), 1.26 – 1.18 (s, 12H), 1.12 (m, 1H), 0.93 – 0.86 (t, *J* 7.4 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.5 (*C*OOR), 150.1, 121.5 (CH=*C*H-COOR), 83.5, 51.7, 33.8, 25.1 (*C*-CH=C), 24.0, 13.7; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 34.1; LRMS (ESI +) m/z [M+H] 269.2 (74%), 290.8 (60%), 237.1 (54%); HRMS (ESI+) m/z calculated $C_{14}H_{26}BO_4$ [M+H] 269.1924 found 269.1933; Chiral HPLC conditions OD-CHIRALCEL column (250 x 4.60 mm) fitted with guard cartridge (50 x 4.6 mm), 25 ºC, 0.40 mL/min, 210 nm, hexane:$^i$PrOH (98:2), $t_R$ = 12.8 min *(S),* $t_R$ = 14.9 min *(R)*.

*Methyl (E)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-2-enoate* **3gii**

Compound **3g** was obtained as a yellow oil (662 mg, 65%) with a $R_f$ = 0.1: IR (neat) $\nu_{max}$ 2976 (s), 1720 (l), 1654 (s), 1458 (s), 1436 (s), 1368 (m), 1316 (m), 1266 (m), 1158 (s), 1142 (l), 1038 (s), 966 (m), 850 (m), 706 (m), 670 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.01 – 6.93 (dt, *J* 15.6, 7.2 Hz, 1H), 5.85 – 5.79 (dt, *J* 15.6, 1.5 Hz, 1H), 3.72 (s, 3H), 2.40 – 2.31 (m, 1H), 2.22 -2.13 (m, 1H), 1.23 (s, 12H,), 1.01 – 0.95 (d, *J* 7.4, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.5(*C*OOR), 150.0, 121.7 (CH=*C*H-COOR), 83.6, 51.7, 35.9, 25.1 (*C*-CH=C), 15.5; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 33.9; LRMS (ESI +) m/z [M+] 236.2 (58%), 235.6 (40%), 254.2 (25%); HRMS (ESI+) m/z calculated $C_{13}H_{24}BO_4$ [M+H] 254.1804 found 254.1817; Chiral HPLC conditions OD-CHIRALCEL column (250 x 4.60 mm) fitted with guard cartridge (50 x 4.6 mm), 25 ºC, 1.0 mL/min, 210 nm, hexane: $^i$PrOH (98:2), $t_R$ = 5.3 min *(S),* $t_R$ = 5.9 min *(R)*.

Methyl (E)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enoate **3iii**

Compound **3i** was obtained as a yellow oil (181 mg, 36%): IR (neat) $\nu_{max}$ 2980 (m), 2944 (s), 2910 (s), 1724 (l), 1658 (m), 1440 (m), 1368 (l), 1324 9 (l), 1274 (l), 1202 (m), 1200 (s), 1140 (l), 1014 (s), 986 (s), 970 (m), 940 (s), 888 (s), 848 (l), 834 (s), 762 (s), 716 (s), 706 (s); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.93 (m, 1H), 5.80 (m, 1H), 3.74 (s, 3H), 2.65 – 2.57 (m, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.11 – 1.10 (m, 3H), 0.95 (d, J 6.7, 1H), 0.89 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.2 (COOR), 157.5, 156.1, 118.0 (CH=CH-COOR), 116.5, 83.2, 83.0, 51.3, 32.5, 29.0, 24.8 (C-CH=C), 22.3, 21.4; $^{11}$B NMR (128 MHz, $CDCl_3$) δ 33.1; LRMS (ESI +) m/z [M+H] 277.1 (100%), 255.1 (62%), 253.9 (10%); HRMS (ESI+) m/z calculated $C_{13}H_{24}BO_4$ [M+H] 254.1804 found 254.1814.

**Other procedures**

(2*E*)-3-(Thiophen-2-yl)prop-2-enal

(2*E*)-3-(Thiophen-2-yl)prop-2-enoic acid (3.0 g, 19.5 mmol) was dissolved in THF (80 mL) and cooled to -78 °C under argon. DIBAL-H (58.5 mL, 1 M THF) was added slowly over 1 hour, and the resulting solution was allowed to react overnight, warming to room temperature. The resulting solution was quenched with saturated potassium sodium tartrate solution (aqueous) and allowed to stir for 1 h. After, the resulting solution was partitioned between EtOAc and the aqueous layer was extracted with EtOAc (3 x EtOAc). The organic phase was separated and dried over $MgSO_4$. After filtration the organic phase was removed under reduced pressure to yield a crude allylic product [(2*E*)-3(thiophen-2-yl)prop-2-en-1-ol)]. In a separate vessel, DMSO (42.9 mmol, 3.0 mL) and DCM (40 mL) were combined under argon and cooled to -78°C). Oxalyl chloride (21.5 mmol, 1.8 mL) was added and the reaction mixture was stirred for 10 min. The crude allylic alcohol [(2E)-3(thiophen-2-yl)prop-2-en-1-ol)] was added (in DCM, 12 mL) to the -78 °C solution, and allowed to stir for 10 min. Triethylamine (97.5 mmol, 13.6 mL) was subsequently added, and the solution allowed to warm to room temperature over 1.5 h. After, the resulting solution was partitioned quenched with water and partitioned between EtOAc and the aqueous layer was extracted with EtOAc (3 x EtOAc). The organic phase was separated and dried over $MgSO_4$. After filtration the organic phase was removed under reduced pressure to yield a crude brown oil. Purification by silica gel chromatography (hexane:EtAcO, 9:1) gave **1j** as a yellow oil (996 mg, 37%).$^1$H NMR (400 MHz, $CDCl_3$): δ 9.63 (d, J = 7.7 Hz, 1H, CH), 7.58 (d, J = 15.6 Hz, 1H, CH), 7.51 (d, J = 5.0 Hz, 1H, CH), 7.37 (d, J = 3.7 Hz, 1H, CH), 7.11 (dd, J = 5.1, 3.6 Hz, 1H, CH), 6.52 (dd, J = 15.6, 7.7 Hz, 1H, CH). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 192.9, 144.4, 139.3, 132.0, 130.4, 128.5, 127.4. LRMS (ESI+) $[M+H]^+$, 138.8. HRMS (ESI+) calculated $[C_7H_6OS+H]^+$ 139.0218, found 139.0246. All spectroscopic and analytical properties are identical with those reported in the literature.[14]

## Acknowledgements

We thank the EPSRC for a Doctoral Training Award (to ADJC).

## Notes and references

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Electronic Supplementary Information (ESI) available: Further experimental details, ReactIR spectra, all $^1$H, $^{13}$C and $^{11}$B NMRs, and X-ray crystallographic details for CCDC 1040392 (**2a**), 1040393 (**2b**), 1040394 (**2e**), 1040395 (**2h**) and 1040594 (**2j**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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